

CEMENT HYDRATION AND STRENGTH DEVELOPMENT – HOW CAN REPRODUCIBLE RESULTS BE ACHIEVED?

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INTRODUCTION

The consistency of high alumina cements with regard to setting and strength development is a key quality feature which distinguishes different grades available in the market. The quality testing of cement must take into account inherent variation of the cement setting behaviour which occurs for example in neat cement testing. When testing castables, the ambient conditions such as temperature, humidity, and the covering of the samples can have an influence on the strength development. This paper discusses results obtained in calorimetric testing of different cement test grogs and of castable testing under practical laboratory conditions with different cement contents and additives in the test castables.

CALCIUM ALUMINATE CEMENT TESTING

Testing of setting behaviour of calcium aluminate cement is carried out by the cement manufacturers, and sometimes also by their customers for quality control purposes. Different test methods are used in the industry. These all provide different results with regard to setting and other cement properties. As a first step the hydration kinetics of a neat cement paste, where only cement and water are used for the test grog, was investigated with a heat flow calorimeter, designed at the University of Erlangen, at a consistent temperature of $23^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$. The calorimetric test method is described in detail by Kuzel¹. Repeated testing of the same CA-14 S cement sample showed a considerable variation of test

results for both length of induction period and time of maximum heat evolution (Fig. 1).

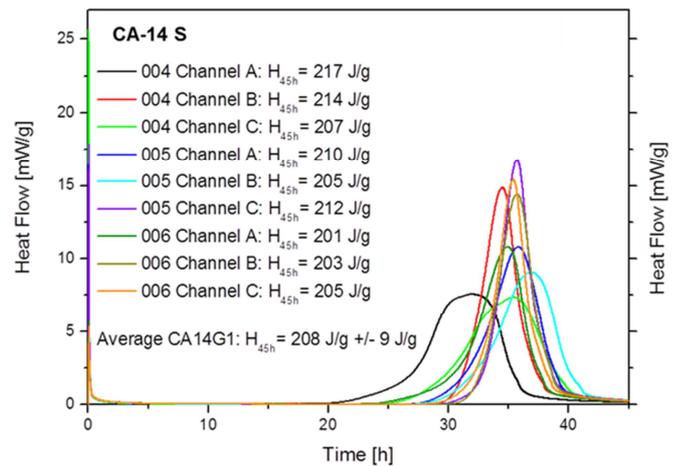


Fig. 1. Repeated heat flow measurements of neat CA-14 cement paste ($T=23^{\circ}\text{C}$, $w/s=0.275$)

This erratic behaviour is typical for iron free 70% Al_2O_3 calcium aluminate cement in general, as illustrated by Götz-Neunhoeffer² in Fig. 2. These tests were performed with the same sample of another cement grade. It is obvious that repeatability of results cannot be achieved with neat cement testing even with the tightly controlled conditions in the calorimeter test method, let alone with neat cement testing by simple temperature and strength development measurements. In addition, the amount of water added to the neat cement is not sufficient for a theoretically complete cement hydration.

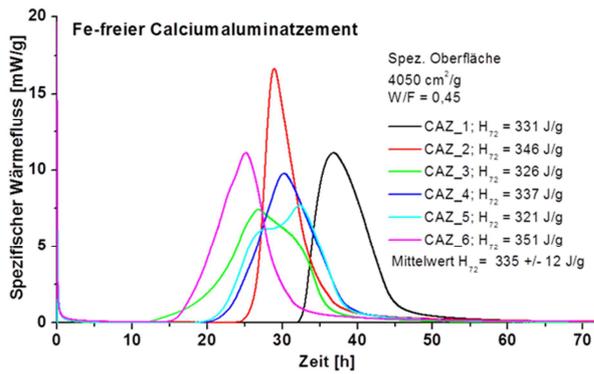


Fig. 2. Heat flow of iron free calcium aluminate cement ($4050 \text{ cm}^2/\text{g}$) hydrated with deionised H_2O (injection method, $T=23^\circ\text{C}$, $w/s=0.45$)¹

Therefore, in practice, test grogs are used where the cement is diluted by inert material in order to improve the repeatability of the test results and also the reproducibility when testing is carried out in different laboratories. Two different well-defined test grogs are used for the quality control of calcium aluminate cements: either the standard silica sand mixture, CEN-Normsand according to EN 196, or Nortab³, a test grog based on the synthetic alumina aggregate tabular alumina.

Fig. 3 shows the results of calorimetric investigations for different tabular alumina additions to the cement. Cements with tabular alumina additions of 50 – 80% were tested. With an addition level of up to 75% tabular alumina, variations in heat flow measurements occur. For the test grog with 80% tabular alumina and 20% cement, good repeatability is achieved. In this case, sufficient water is also provided for the cement to react. Almatix Nortab testing³, which has been carried out for many years, with a tabular alumina/cement ratio of 80/20 has proved to be a suitable test method for calcium aluminate cements.

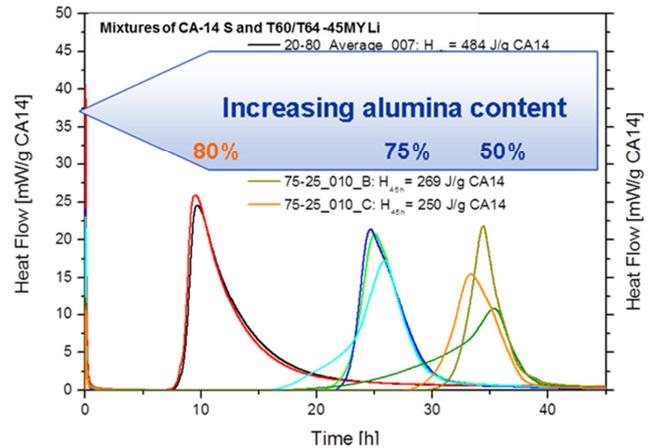


Fig. 3. Heat flow measurements of cement diluted with different amounts of tabular alumina filler ($T=23^\circ\text{C}$, $w/s=0.275$)

IMPACT OF AMBIENT TEMPERATURE ON SETTING

When considering the reliability of testing not only is the test mixture of importance, but also the ambient conditions such as temperature. Calorimetric measurements of 80% tabular alumina and 20% cement, which are, for standard tests at the University of Erlangen, performed at 23°C , were also tested at 20°C to investigate the impact of a small temperature variation on the cement hydration. The heat flow curves for both temperatures are shown in Fig. 4. The reduction of ambient temperature of only 3°C during the hydration test has a clear retarding effect of about six hours on the main hydration peak, although the shape of the curve does not change. This indicates that the same reaction kinetics take place during the main reaction.

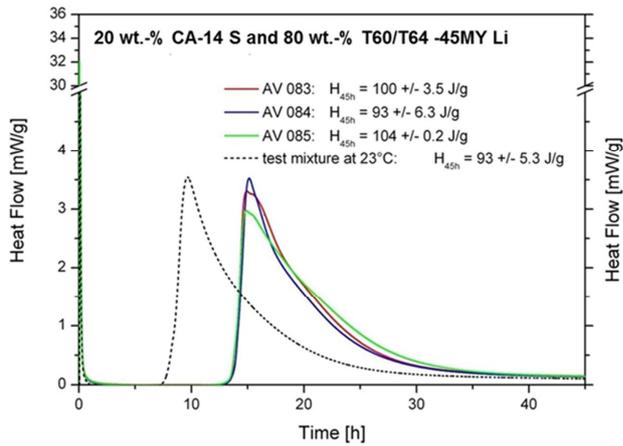


Fig. 4. Hydration of 20% CA-14 and 80% tabular alumina filler at 20°C vs. 23°C (w/s=0.275)

A similar trend has been observed in a series of tests performed in the Almatix laboratory where setting behaviour of different castables was tested at 20°C ambient temperature in the laboratory vs. 20°C in the climate cabinet. When compared to the curing process in an air-conditioned room, where the heat released results in an overall heating of the test block, the heat released in the climate cabinet is dissipated immediately and the exothermic reaction is suppressed and also retarded.

The exothermic profiles of two different low cement castables cured at 20°C in the room and in the climate cabinet are given in Fig. 5. The temperature increase right at the start is due to heat developed in the castable during the mixing by friction. As the cement hydration is very sensitive, even under well-defined conditions, the repeatability will become worse under less controlled ambient temperatures in the laboratory, for example without air conditioning.

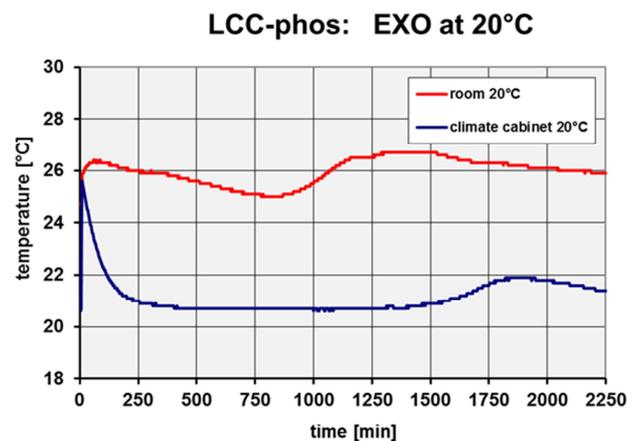
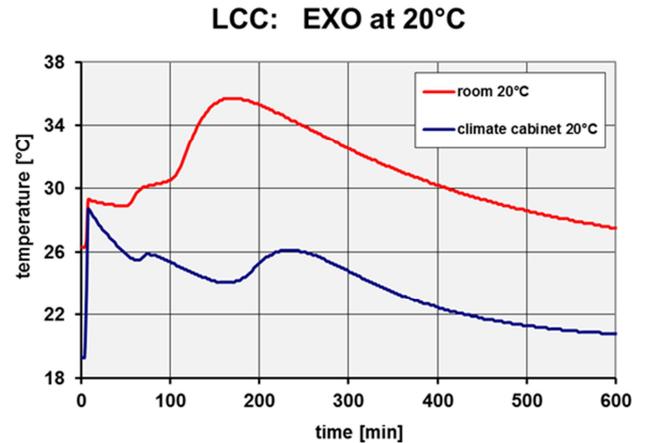


Fig. 5. Exothermic reaction of two low cement castables at 20°C in the laboratory and in a climate cabinet: later hydration in the climate cabinet

IMPACT OF AMBIENT TEMPERATURE ON STRENGTH

It is well known that not only is the setting behaviour of refractory castables impacted by the curing temperature but also is the strength development. This is because the strength depends on the degree of hydration achieved during curing.

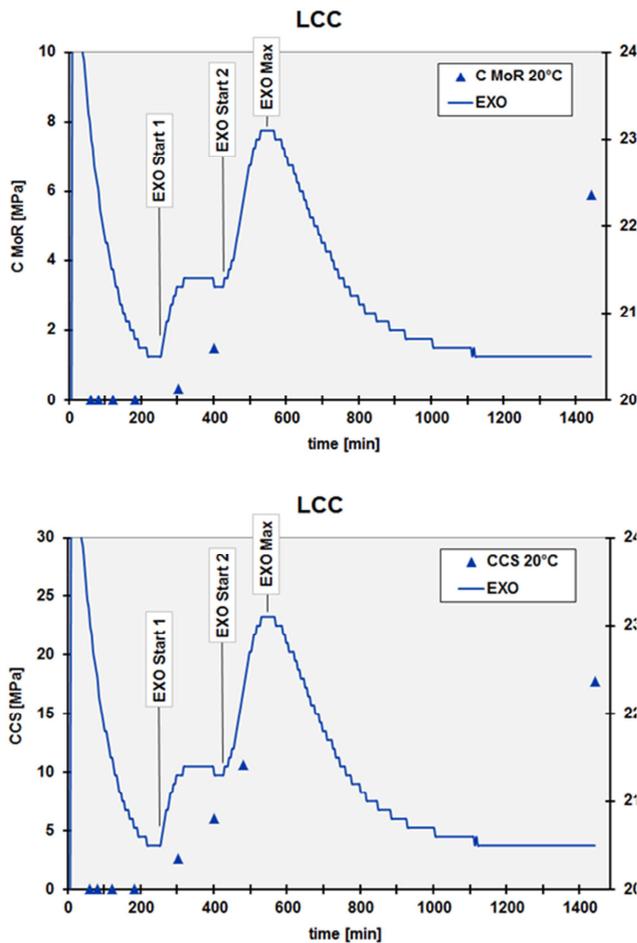


Fig. 6. Correlation of the exothermic reaction and strength development at 20°C of a low cement castable

Single measurements of tabular alumina low cement castable illustrate the correlation of the exothermic setting curve and the strength development (Fig. 6) and also the ultrasonic setting curve and the strength development (Fig. 7). The strength development starts between the first and the second rise of the exothermic curve (EXO start 1 and 2) simultaneously with the increase in ultrasound velocity.

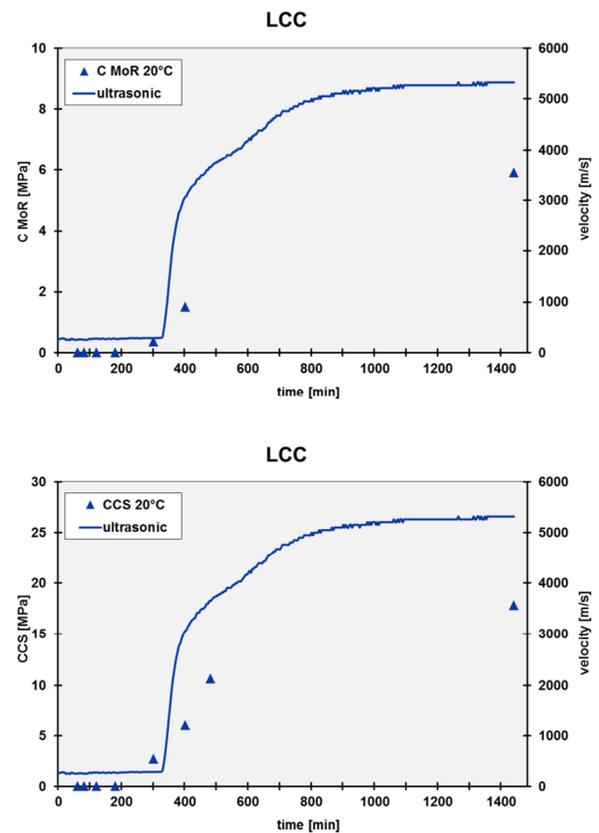


Fig. 7. Correlation of the ultrasonic setting and strength development at 20°C of a low cement castable

Low temperature curing has a negative effect on the strength development because of two effects. The cement hydration is retarded at low temperatures and therefore less strength develops. Also the calcium aluminate hydrates formed during hydration at low temperatures contain more water and have a lower density when compared to hydrates formed at higher curing temperatures⁴⁻⁶. Previous investigations from Buhr et al.⁷ on strength development at 5 and 20°C demonstrate that calcium aluminate cements inherently develop less strength during curing at low ambient temperatures. This is shown in Fig. 8.

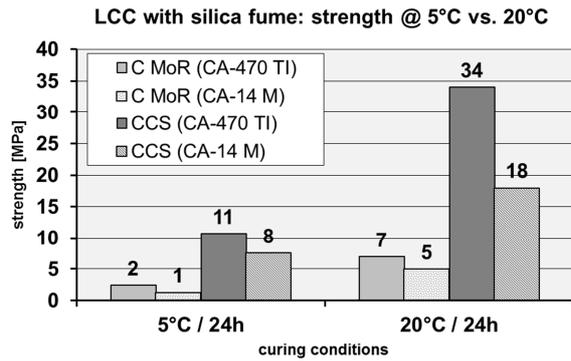


Fig. 8. Cold crushing strength of test castables after curing at 5 and 20°C⁶

IMPACT OF CURING CONDITIONS ON STRENGTH

Strength development during curing is an important consideration during the development work and quality control of refractory castables in addition to the rheological properties during mixing and placement. The significant influence of temperature on the strength development has been discussed before. In addition, the samples may be covered during curing or be exposed to air drying. The impact of different curing methods was investigated for six test castables based on tabular alumina aggregate with cement contents of 0 – 15%.

TEST CASTABLES

The conventional castable (CC) contained 15% CA-25 C. Three low cement castables were selected, containing 5 – 6% CA-14 S or CA-270. Two of the three were pure alumina castables – one containing ADS/W (LCC), the other with sodium polyphosphate (Budite 8H) and sodium citrate as additives (LCC-phos). The third was a silica fume containing mix with M-ADS/W (LCC-fume). The ultralow cement castable was a silica fume free mix containing 3% CA-270 (ULCC). For the no-cement formulation 3% Alphasond 300 was used as the hydratable alumina binder (NCC). The

composition of the test castables is given in Tab. I.

Tab. I. Composition of test castables

Component	Castable	CC	LCC	LCC-phos	LCC-fume	ULCC	NCC
Component		%	%	%	%	%	%
T60/T64	up to 6 mm	70	69	74	74	69	75
	-45 MY Li	5	9	9	8	11	2
	-20 MY						7
Calcined Alumina	CT 9 FG	10					
Reactive Alumina	CTC 50		17			17	
	CTC 20				10		
	CL 370			4.5			13
	RG 4000			6.5			
silica fume	Elkem 971U				3		
Binder	CA-25 C	15					
	CA-14 S			6	5		
	CA-270		5			3	
	AB 300						3
Additives	ADS/W		1.0			1.0	1.0
	M-ADS/W				1.0		
	Budite 8H			0.05			
	Sodium citrate			0.03			
Water		7.8	4.5	5.5	4.3	4.5	4.5

EXPERIMENTAL

The different castables were wet mixed in 5 kg batches using a Hobart A200 planetary mixer at speed 1 for 4 minutes. Test bars were cast immediately after mixing and cured under different conditions for 24 hours, and in selected cases for 48 hours. For the curing process the test bars were stored as follows:

Exposed to air drying: The moulds with the test bar were stored in the laboratory at 20°C for 24 hours without a cover.

Covered: The moulds with the test bar were stored in the laboratory at 20°C for 24 hours and were covered with a Plexiglass-plate.

In a plastic bag: The moulds with the test bar were stored in a securely closed plastic bag in the laboratory at 20°C.

In the climate cabinet: The moulds with the test bar were stored in a climate cabinet at 20°C and 90% relative humidity for 24 hours.

According to European standard DIN-ISO 1927 part 1-8: The moulds with the test bar were stored in a climate cabinet at 20°C and 90% relative humidity for 24 hours. The bars were then de-moulded and stored for a further 24 hours in the climate cabinet under the same conditions.

Cold crushing strength was determined after 24 hours. The cured strength after 48 hours was also measured for the castables CC, LCC-phos, and NCC. In addition to the cured strength, the weight loss of the castable bars during curing was determined after 2, 4, 6, 8 and 24 hours. This data was used later for calculation of the water/cement (w/c) ratio and water/Alphabond-binder (w/b) ratio after the different curing steps.

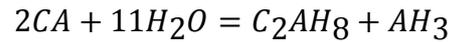
CRITICAL WATER/CEMENT RATIO

In order to achieve the desired strength development during curing sufficient water should be provided for the cement hydration. In technical systems with coarse aggregates, fine fillers, and cement, sufficient water is also needed for the required flow behaviour and placing properties of the mix. However, too high water demands are disadvantageous for the refractory properties in use. The minimum water demand required for a theoretically complete cement hydration can be calculated and is known as critical water/cement ratio.

The critical water/cement ratio depends on the nature of the hydrates formed⁸. Scrivener et al.⁸ state a critical water/cement ratio of about 0.7 for calcium aluminate cement containing about 50% CA for low temperatures when CAH₁₀ is present, and 0.35 for high temperatures when C₃AH₆ and gibbsite (AH₃) are formed. As curing

trials for this test series were performed at 20°C the critical water/cement ratio was calculated for C₂AH₈ and AH₃, which can be assumed to be the dominant hydrate phases formed in this temperature range. Here, a critical w/c ratio of about 0.6 for a theoretically complete cement hydration is obtained from the calculation below.

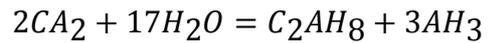
Calculation for CA (C = CaO, A = Al₂O₃, H = H₂O; molecular weight g/mol):



$$316 + 198 = 358 + 156 = 514$$

$$\frac{w}{c} = \frac{198}{316} = 0.63$$

Calculation for CA₂:



$$520 + 306 = 358 + 468 = 826$$

$$\frac{w}{c} = \frac{306}{520} = 0.59$$

RESULTS AND DISCUSSION

Fig. 9 shows the w/c and w/b ratios for the different test castables and curing methods over curing time of 24 hours. The red area indicates the critical w/c ratio which was set at 0.5-0.6 based on the calculation above and taking into account that complete cement hydration in technical systems normally does not occur. The critical water/Alphabond ratio was also set at 0.5-0.6. Complete AH₃ formation would require w/b = 0.53, but at 20°C an amorphous aluminium hydrate phase is formed which may contain more water when compared to crystallised AH₃.

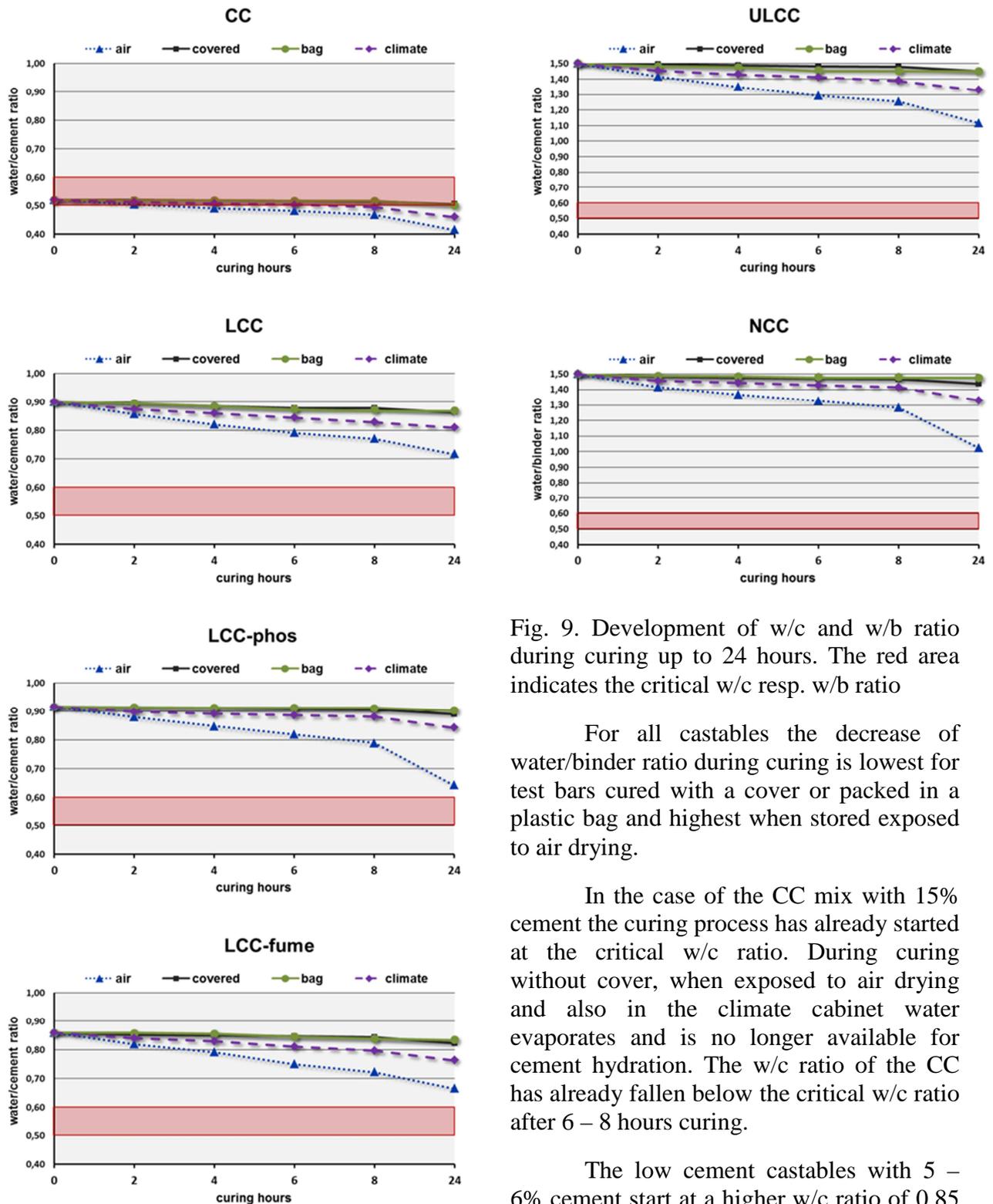


Fig. 9. Development of w/c and w/b ratio during curing up to 24 hours. The red area indicates the critical w/c resp. w/b ratio

For all castables the decrease of water/binder ratio during curing is lowest for test bars cured with a cover or packed in a plastic bag and highest when stored exposed to air drying.

In the case of the CC mix with 15% cement the curing process has already started at the critical w/c ratio. During curing without cover, when exposed to air drying and also in the climate cabinet water evaporates and is no longer available for cement hydration. The w/c ratio of the CC has already fallen below the critical w/c ratio after 6 – 8 hours curing.

The low cement castables with 5 – 6% cement start at a higher w/c ratio of 0.85 - 0.9 immediately after mixing. LCC's also show a decline of the w/c ratio over time especially for the uncovered bars cured

whilst exposed to air. Even for this curing method the critical w/c ratio is not reached after 24 hours curing.

The ULCC containing only 3% cement and the NCC with 3% Alphasol were mixed at a water/binder ratio of about 1.5. Even after 24 hours curing the w/b ratio of the ULCC and NCC is far above the critical w/c / w/b ratio. In this case the amount of water which is not needed for cement hydration is quite high, this is especially the case for the test bars cured while covered or sealed in a bag.

Scrivener et al.⁸ states that water added in excess of the critical w/c = 0.35 will not be combined into the stable hydrates and will only contribute to the porosity of the paste, with an adverse effect on strength. Therefore a high amount of excess water in ULCC and NCC can have a negative impact on cured strength. The decrease of strength by moisture contained in hydraulically bonded pre-cast shapes was also discussed in previous studies for refractory materials^{9,10}

Fig. 10 shows how the strength properties of the different curing methods relate to each other. The strength values of the test bars exposed to air drying are defined as zero and the difference in values of the other test bars are shown in percentage terms.

The strength of CC is highest when cured covered, in a plastic bag or at high relative humidity. Low strength is achieved for samples cured exposed to air drying. As the w/c ratio of 0.42 after 24 hours is below the critical limit it can be assumed that a part of the cement has not hydrated because of insufficient water availability. Strength testing after 48 hours shows no further increase and confirms this assumption.

LCC and LCC-fume achieve comparable strength levels for all curing

methods. Whether part of the mixing water is able to escape or kept in the test bar with a covering, it does not impact the strength.

The strength properties for the LCC-phos after 24 hours look worse and are caused by a very long setting as shown in the exothermic reaction (fig. 5). The maximum temperature development occurred after more than 24h. Therefore the 48h strength values should be taken into account instead. These are then comparable to LCC and LCC-fume.

LCC's have sufficient water available for a theoretically complete cement hydration even after 24 hours curing when exposed to air drying and they do not reach the critical w/c ratio. The excess of water which is available when a covering is applied during curing is within a reasonable range and does not show a negative impact on strength.

The ULCC shows the reverse effect when compared to CC. This effect is even more pronounced with the NCC. Only a small part of the mixing water is required for the hydration of the cement or the Alphasol binder. When the excess water which is not contributing to the hydration cannot evaporate due to covering or high relative humidity, the strength of the test bar is decreased by the presence of a high amount of excess moisture as described in the literature^{9,10}.

For a proper green strength development of ULCC and NCC - type castables, it is advantageous if some of the excess water is removed from the system. Curing exposed to air can be taken as the most favourable curing method for ULCC and NCC. Practical experience with NCC pre-cast shapes, which were covered during curing, resulted in inferior performance when compared to pre-cast shapes which

were cured uncovered and achieved good life. That correlates with these laboratory results.

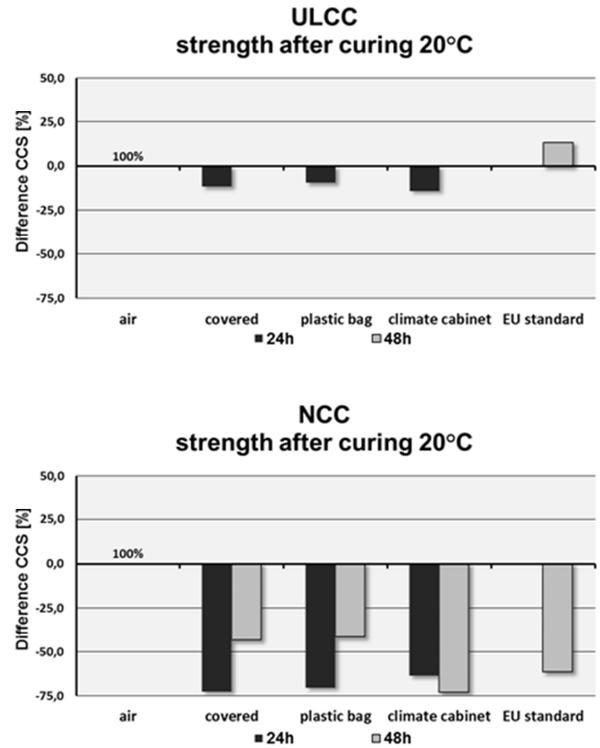
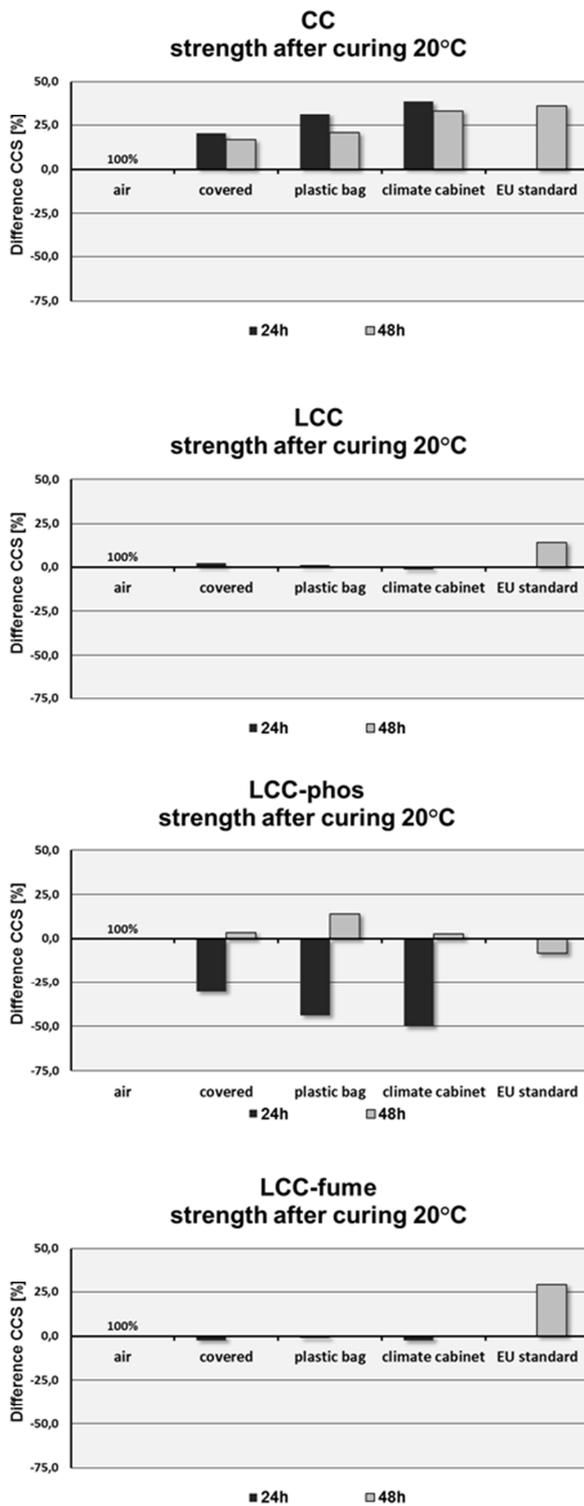


Fig. 10. Difference in cold crushing strength after 24 and 48 hours curing at 20°C by applying different curing methods

CONCLUSION

For quality control of calcium aluminate cements, the use of test grog, where the cement is diluted by inert filler, is an essential requirement to achieve repeatable and reproducible results. The repeatability of the hydration reaction of Nortab mixture containing 80% tabular alumina and 20% cement is best when compared to neat cement testing and lower filler additions to the cement. In addition to the test method a strict control of the ambient temperature is required for the quality control of cement. Even small temperature differences from 20 to 23°C can significantly change the timing of the main cement reaction. A retarding effect has been observed for measurements performed in the climate cabinet when compared to the

laboratory. In the climate cabinet the heat released is dissipated and is not available to heat the castable and accelerate the setting.

Calcium aluminate cements inherently develop less strength during curing at low temperatures. In addition the cured strength is impacted by the curing method. For the strength development of high cement containing castables it is beneficial to cure the pieces with a covering to ensure that sufficient water is available for the cement hydration. A different curing method is recommended for ultralow and no cement castables where only a small part of the mixing water is required for the cement hydration. The removal of some of the excess water by curing the pieces whilst exposed to air improves the green strength when compared to the other curing methods. A difference between the different curing methods was not observed for low cement castable types. Well controlled ambient conditions and tailored curing conditions are key factors to achieve improved green strength properties and performance in both laboratory and application.

The curing conditions described in the European standard DIN-ISO 1927 part 1-8 have in the past been developed based upon the optimum conditions for conventional, high cement containing castables. The investigation shows that ultralow and non-cement castables would require different conditions to achieve the best results. Low cement castables proved to be most robust with regard to the curing conditions and could be considered the least critical for a re-evaluation of the norm.

REFERENCES

1. H.J. Kuzel, "An efficient conduction-type calorimeter", TIZ 108 (1984) 46-48 (50-51).

2. F. Götz-Neunhoeffler, "Modelle zur Kinetik der Hydratation von Calciumaluminatzement mit Calciumsulfat aus kristallchemischer und mineralogischer Sicht", Erlanger Forschungen, Reihe B, Naturwissenschaften und Medizin, Band 29, ISBN: 3-930357-78-X, (2006), S. 80-81.
3. Calcium Aluminate Cements – Cement Test Methods, Almatris GP-RCP/006/R06/0812, available under www.almatis.com.
4. G.V. Givan et al., "Curing and firing high purity calcium aluminate-bonded tabular alumina castables", Ceramic bulletin, Vol 54, No 8, 1975, 710-713.
5. R.E. Roesel, G. MacZura and P.T. Rothenbuehler, "Calcium aluminate cements for high strength refractory monolithics", Interceram 31, No 5, 1982, 519-523.
6. J.E. Kopanda and G. MacZura, "Production processes, properties, and applications for calcium aluminate cements", Alumina Science and Technology Handbook, ed. By LeRoy D. Hart, American Ceramic Society, 1990, 171-183.
7. A. Buhr et al., "New results for CA-470 TI temperature independent cement – robustness against low temperature and impurities", Proceedings of UNITECR '09, 2009, October 13-16, Salvador, Brazil, paper #051.
8. K.L. Scrivener and A. Capmas, "13 – Calcium Aluminate Cements", Lea's Chemistry of Cement and Concrete (Fourth Edition), Butterworth-Heinemann, 2004, 713-782.
9. D. Gierisch et al., "Moisture pick up and strength of hydraulically bonded pre-cast shapes", 51st International Colloquium on Refractories, Aachen, Germany, 2008, 58-63
10. G. Routschka, R. Krebs, K. Hombach, "Influence of moisture pick-up on strength of refractory product", INTERCERAM, No.5, 1986, pp 31-35.